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PATENT
2185-0612P

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant: Katsuhiko NAMBA et al. Conf.: 2564
Appl. No.: 10/046,742 Group: 1752
Filed: January 17, 2002 Examiner: THORNTON
For: CHEMICAL AMPLIFYING TYPE POSITIVE RESIST
COMPOSITION

LETTER SUBMITTING SUPPLEMENTAL
DECLARATION UNDER 37 C.F.R. 1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

March 16, 2005

Sir:

Enclosed is a Supplemental Declaration submitted under 37 C.F.R. 1.132 (hereinafter the "Supplemental Nakanishi Declaration"). The Supplemental Nakanishi Declaration includes comparisons between the present invention and compositions based on Examples 7 and 8 of Barclay '086 (USP 6,492,086). The Supplemental Nakanishi Declaration is being submitted in response to the request by the Patent Examiner for such a comparison as indicated in paragraph (11) at page 9 of the Final Office Action dated September 20, 2004.

It is requested that the Supplemental Nakanishi Declaration be fully considered and entered of record in connection with the above-identified application. It is submitted that the Supplemental Nakanishi Declaration provides significant evidence further establishing the patentability of the present claims over Barclay '086.

If any questions arise regarding the above matters, please contact Applicant's representative, Andrew D. Meikle (Reg. No. 32,868), in the Washington Metropolitan Area at the phone number listed below.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. § 1.16 or under § 1.17; particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By


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Attachment: Supplemental Nakanishi Declaration



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of Katsuhiko NAMBA et al.

Serial No. 10/046,742

Filed : January 17, 2002

Group Art Unit : 1752

Examiner : THORNTON, YVETTE C

CHEMICAL AMPLIFYING TYPE POSITIVE RESIST
COMPOSITION

* * * * *

DECLARATION

I, Junji NAKANISHI, residing at 5-1,
Otowayakude-cho, Yamashina-ku, Kyoto-shi, Kyoto, 607-8076,
Japan, declare and say:

that I graduated and obtained Master Degree from Graduate School
of Engineering, Osaka Prefecture University in March, 1999.

Since April, 1999 to the present, I have been employed by
Sumitomo Chemical Co., Ltd., assignee of the above-identified
application, and engaged in research and development in the field of
syntheses of resins and of product developments for photoresist
compositions;

that I am one of the inventors of the invention of the
above-identified application; and

that in order to examine whether the relationship between the flexibility imparting effect on a film and the preventing effect on scum production is present or not, and also to show unexpected result obtained by the present composition, I beg to submit the following experimental data which have been obtained under my supervision:

Experiments

With Component X defined below, the experiments were performed approximately according to Examples 7 and 8 in US 6,492,086 B1 except that the compound of the formula (III) was used as the acid generating agent instead of di-t-butyl phenyl iodonium camphorsulfonate, and that p-hydroxystyrene / 2-ethyl-2-adamantyl methacrylate copolymer was used as the resin instead of p-hydroxylstyrene / 2-methyl-2-adamantyl methacrylate copolymer.

1. MATERIALS

(1) Resins

i) Resin

Resin was synthesized according to the method described in the present specification “(2a) Synthesis of copolymer of 2-ethyl-2-adamantyl methacrylate and p-acetoxystyrene (30:70)” and “(2b) Synthesis of copolymer of 2-ethyl-2-adamantyl methacrylate and p-hydroxystyrene (30:70)” from page 15, line 12 to page 16, line 18.

The resin had a weight-average molecular weight (M_w) of about 8600

and a degree of dispersion of 1.9 (GPC method: in terms of polystyrene), and revealed a copolymerization ratio of about 30:70 measured by a nuclear magnetic resonance ($^{13}\text{C-NMR}$) spectrometer.

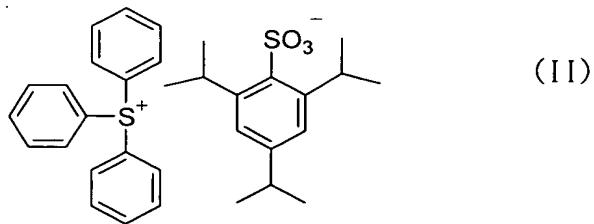
(2) Component X

Among the examples of the plasticizer, at column 35, lines 11-16 in Nakamura et al., the following compounds are selected as Compound X based on the criteria of their commercial availability.

- (a) polypropylene glycol (M_w : about 2000) (in Example 1)
- (b) polyacrylic acid (M_w : about 2000) (in Comparative Example 1)
- (c) tri-n-butyl citrate (in Comparative Example 2)
- (d) diethyl phthalate (in Comparative Example 3)
- (e) di-n-butyl phthalate (in Comparative Example 4)
- (f) di-n-hexyl phthalate (in Comparative Example 5)
- (g) di(2-ethylhexyl) phosphate (in Comparative Example 6)
- (h) tri-n-butyl phosphate (in Comparative Example 7)
- (j) tricresyl phosphate (in Comparative Example 8)
- (k) tris(2-ethylhexyl) phosphate (in Comparative Example 9)
- (l) none (in Comparative Example 10)

(3) Acid generating agents

Acid generating agent of the following formula (II)



(4) Quencher

tetrabutylammonium lactate

(5) Solvent

ethyl lactate

(6) Surfactant

Silwet L-7604 (distributor: Dow Corning Toray Silicone Co., Ltd.)

2. Examples and Comparative Examples

All Part(s) and % shown in Example and Comparative Examples are by weight.

(1) Preparation of Resist Composition

94.4 parts of Resin, 4.72 parts of Acid generating agent, 0.38 part of Quencher, and 700 parts of Solvent were mixed to provide a solution. This solution was further filtrated through a fluorine resin filter having a pore diameter of 0.2 μm to prepare a resist solution.

To this resist solution was added Component X shown above in an amount of 1% based on the resin mixture to obtain resist solution containing Component X.

(2) Evaluation of Resist Solution

On a silicon wafer, an anti-reflection film [“DUV-42” manufactured by Nissan Chemical Industries. Ltd.] was applied under pre-bake conditions of 215 °C and 60 seconds to give a thickness of 0.06 µm. Then, each of the resist solution containing Component X was spin-coated on this, followed by pre-baking on a proximity hot plate under conditions of 110°C and 60 seconds to form a resist film having a thickness of 0.40 µm. A wafer carrying thus formed resist film was exposed using a KrF excimer stepper [“NSR-2205EX12B” manufactured by Nikon Corp., NA=0.55, σ =0.80] via masks having various forms and dimensions. Then, PEB was conducted under conditions of 110°C and 90 seconds on a hot plate, further, puddle development was conducted for 60 seconds with a 2.38% tetramethylammonium hydroxide aqueous solution. Patterns after development were observed by a scanning electron microscope, and sensitivity, resolution and presence of scum were checked as described below.

Results are shown in Table 1.

Film penetrating sensitivity: This was indicated by the minimum exposure required for film penetration of 2 mm square open field after exposure and development. This is represented by Eth.

Effective sensitivity: This was indicated by exposure amount at which 0.20 µm line and space pattern was 1:1. This is represented by Eop.

Presence of scum: A wafer carrying patterns formed at exposure at

which 0.20 μm line and space pattern was 1:1 was observed from the upper surface using a scanning electron microscope, and presence of scum (residue) at exposed parts was checked. Observation of one or more scum was represented by \times , and observation of no scum was represented by \circ .

Resolution: This was indicated by the minimum dimension of line and space pattern separating at exposure of effective sensitivity.

Table 1

Example No.	Component X	Sensitivity		Resolution (mm)	Presence of scum		
		(mJ/cm ₂)					
		Eth	Eop				
Exp. 1	(a)	9	28	0.17	\circ		
Comp.Exp.1	(b)	Unable to evaluate*					
Comp.Exp.2	(c)	9	28	0.17	\times		
Comp.Exp.3	(d)	9	29	0.17	\times		
Comp.Exp.4	(e)	9	28	0.17	\times		
Comp.Exp.5	(f)	9	28	0.17	\times		
Comp.Exp.6	(g)	11	35	0.20	\times		
Comp.Exp.7	(h)	9	28	0.17	\times		
Comp.Exp.8	(j)	9	28	0.17	\times		
Comp.Exp.9	(k)	9	28	0.17	\times		
Comp.Exp.10	(l)	9	30	0.17	\times		

*:Unable to evaluate due to the insolubility of Component X in the solvent

3. Discussions and Conclusions

Example 1 (Exp. 1) corresponds to the present invention and contains polypropylene glycol. Comparative Example 10 (Comp.Exp. 10) contains no Component X. Apparent from the comparison of the results of Example 1 and

Comparative Example 10, the present invention has a great preventing effect on scum production.

On the other hand, none of Comparative Examples 1 to 9 (Comp.Exp. 1 to 9) has such preventing effect on scum production.

From the results of Example 1 and Comp.Exp. 1 to 9 above, I can conclude that the flexibility imparting effect on a film and the preventing effect on scum production are totally different and that no relationship exist therebetween, and that resist composition having good preventing effect on scum production can be achieved only by the one containing polypropylene glycol among the above Component Xs, which are well known as plasticizers.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United State Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 2 nd day of March 2005.

Junji Nakanishi
Junji NAKANISHI